

PATENT SPECIFICATION

(11) 1253 062

1253 062

NO DRAWINGS

- (21) Application No. 53112/68 (22) Filed 8 Nov. 1968
 (31) Convention Application No. 681 919 (32) Filed 9 Nov. 1967 in
 (33) United States of America (US)
 (45) Complete Specification published 10 Nov. 1971
 (51) International Classification C 08 g 41/02
 (52) Index at acceptance

C3R 22C1 22C10 22C11 22C12 22C13P 22C13X 22C14A
 22C14B 22C15 22C21 22C22 22C23 22C24 22C25
 22C28X 22C39A 22C33X 22C5A 22C5B1 22C5B2
 22C6A1 22C6AX 22C6B 22C6X 22C8P 22C8R
 22D1A2 22D1AX 22D2A1 22D2A2 22D2AX 22D3D1
 22D3D2 22D3D3 22D3DX 22L1A 22L1B 22L2C1
 22L2CX 22L2X 22L3A 22L4C 22L6F 22MX 22N1A
 22N1B 22P2 22T1 22T2



(54) POLYAMIDE COMPOSITIONS

PATENTS ACT 1949

SPECIFICATION NO. 1,253,062

In pursuance of Section 8 of the Patents Act, 1949, the Specification has been amended in the following manner:-

Page 2, line 1, page 10, line 40, *after polyamide insert* (as herein defined)

Page 2, lines 25 and 26, *delete* Polyamides usable herein include two broad categories. One category *insert* As used in relation to the present invention, 'polyamide' means 'a polymer of one or more lactams or a polymer formed by condensing one or more diacids with one or more polyamines'. The first category

Page 2, line 33, *after* ϵ caprolactum *insert* .Lactum monomers in addition to ϵ caprolactum

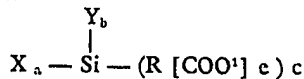
Page 2, line 36, *for* caprillactum, cyclo decanone *read* capryllactum cyclodecanone

THE PATENT OFFICE

21 April 1972

R 9765/1

meric composition comprising an organic poly-
 meric material and a mineral reinforcing agent,
 the latter being chemically bound to the poly-
 meric material by a silane having the general
 formula:



in which X is a halogen atom or an alkoxy
 group, each of Y and Z is a hydrogen atom or
 a hydrocarbyl group, R is a alkylene group
 having at least 10 carbon atoms, an alkenylene
 group, or a cycloalkene group, a is 1, 2, or 3,
 b is 0, 1 or 2, c is 1, 2 or 3 and the sum of a,
 b, and c is 4, e is 1 when R is an alkylene or
 alkenylene group, or 1, 2 or 3 when R is a

aromatic hydrocarbons can be incorporated
 with a base catalysed, substantially anhydrous
 lactam polymerisation.

It has been found that these unexpected
 advantages can be obtained only if both criteria
 are observed; thus, adding the appropriate
 quantity of inorganic filler without the halo-
 genated aromatic hydrocarbon in the prescribed
 amount does not provide a flame resistant com-
 position; likewise, adding the appropriate
 quantity of halogenated aromatic hydrocarbon
 without the inorganic filler in the prescribed
 amount also does not provide a flame
 resistant composition.

Accordingly, therefore, the present invention
 provides a flame resistant polymer composition
 comprising:

SPECIFICATION AMENDED - SEE ATTACHED SLIP

PATENT SPECIFICATION

(11) 1 253 062

1 253 062

NO DRAWINGS

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 22C6A1 22C6AX 22C6B 22C6X 22C8P 22C8R
 22D1A2 22D1AX 22D2A1 22D2A2 22D2AX 22D3D1
 22D3D2 22D3D3 22D3DX 22L1A 22L1B 22L2C1
 22L2CX 22L2X 22L3A 22L4C 22L6F 22MX 22N1A
 22N1B 22P2 22T1 22T2



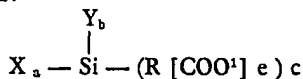
(54) POLYAMIDE COMPOSITIONS

(71) We, MONSANTO COMPANY, a corporation organised under the laws of the State of Delaware, United States of America, of 800, North Lindbergh Boulevard, St. Louis 66, State of Missouri, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to flame resistant polyamide compositions, and to a polymerization process for preparing them.

Reinforced thermoplastic resinous compositions are already known, for instance in our British Patent No. 1,069,752 there are described reinforced thermoplastic resinous compositions comprising an organic thermoplastic resinous material which is free from aliphatic unsaturation, and an inorganic reinforcing agent, the latter being bound to the organic thermoplastic resinous material through the groups of a coupling agent.

Furthermore, in our British Patent No. 1,097,678 there is described a reinforced polymeric composition comprising an organic polymeric material and a mineral reinforcing agent, the latter being chemically bound to the polymeric material by a silane having the general formula:



in which X is a halogen atom or an alkoxy group, each of Y and Z is a hydrogen atom or a hydrocarbyl group, R is a alkylene group having at least 10 carbon atoms, an alkenylene group, or a cycloalkene group, a is 1, 2, or 3, b is 0, 1 or 2, c is 1, 2 or 3 and the sum of a, b, and c is 4, e is 1 when R is an alkylene or alkenylene group, or 1, 2 or 3 when R is a

cycloalkane group.

Many halogenated organic compounds are used to flame proof resinous materials. Many of these additives are effective in increasing the flame resistance of polyamides. Unfortunately, to achieve a beneficial reduction in flame susceptibility in polyamides, the flame-retardant additives must usually be added in such large quantities that mechanical properties are adversely affected, and the cost of the resultant product dramatically increased. Further, because of their inhibiting effect on the polymerization many conventional flame retardant additives cannot be incorporated into a lactam monomer system which is to be polymerised via a base-catalysed, substantially anhydrous, reaction.

It has now unexpectedly been found that if two criteria are observed, one with respect to the minimum percentage by volume of an inorganic filler, the other with respect to the range of percentage by weight of a halogenated aromatic hydrocarbon, then flame resistant compositions can be prepared with good mechanical properties and at reasonable cost. Aromatic hydrocarbons can be incorporated with a base catalysed, substantially anhydrous lactam polymerisation.

It has been found that these unexpected advantages can be obtained only if both criteria are observed; thus, adding the appropriate quantity of inorganic filler without the halogenated aromatic hydrocarbon in the prescribed amount does not provide a flame resistant composition; likewise, adding the appropriate quantity of halogenated aromatic hydrocarbon without the inorganic filler in the prescribed amount also does not provide a flame resistant composition.

Accordingly, therefore, the present invention provides a flame resistant polymer composition comprising:

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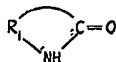
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- (a) a polyamide;
 (b) at least 20% by volume of the composition of an inorganic filler; and
 (c) from 8% to 35% by weight of the polyamide of a polyhalogenated aromatic hydrocarbon, or a mixture thereof with antimony oxide.

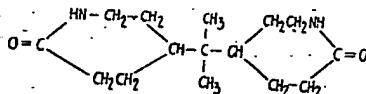
According to a further feature of the invention there is provided a process for the production of a flame resistant polymer composition according to this invention wherein a mixture containing a monomeric lactam, and capable of being polymerized to form component (a), at least 20% by volume of an inorganic filler and from 8% to 35% by weight of the lactam of a polyhalogenated aromatic hydrocarbon, is prepared and subjected to a base-catalyzed, substantially anhydrous polymerization of the lactam.

It is to be understood that a mixture of polyhalogenated aromatic compounds may be used and that the expression "flame retardant material" used in this specification includes such mixtures.

Polyamides usable herein include two broad categories. One category includes the poly-lactams produced by the polymerisation of lactam monomers of the formula



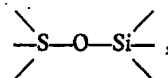
- wherein R₁ is an alkylene group having from 3 to 12 carbon atoms, and preferably from 5 to 12 carbon atoms. A preferred monomer is ϵ -caprolactam include α -pyrrolidone, piperidone, valerolactam, caprolactams other than the ϵ -isomer, methyl cyclohexanone isoximes, caprillactam, cyclo decanone isoxime, lauryllactam. A preferred polyamide is polycaprolactam, commonly known as nylon 6. Other polylactams usable herein include polyundecanolactam and polylauryllactam. Also included are copolymers of two or more of the above, or similar lactam monomers as well as copolymers of mixed lactam monomers. Examples include copolymers of caprolactam with capryllactam, copolymers of caprolactam with lauryllactam and copolymers of pyrrolidone with piperidone or caprolactam as well as copolymers of a lactam with a bislactam having a formula such as the following:



The second category of polyamides comprises those polymers formed by the condensation

polymerization of dicarboxylic acids with diamines, one of the most significant polymers being polyhexamethylene adipamide (nylon 6,6). Other related polyamides include those formed from polyamines such as propane-diamine, hexamethylenediamine and octamethyldiamine and polycarboxylic acids such as adipic acid, pimelic acid, suberic acid, sebacic acid and dodecanedioic acid. One notable example is polyhexamethylene sebacamide (nylon 6,10). Also included are copolymers or mixtures of polyamides of the two above categories. The copolymers or mixtures can consist of combinations of the two forms of polyamides with each other or with other compatible resin systems. The copolymers or mixtures of this invention preferably contain at least 50% by weight polyamide. Most of the preferred compositions will contain at least 90% by weight polyamide in the resin phase. Examples of resins which can be mixed with polyamides to form a blend include polypropylene, polyethylene, polystyrene, polyacrylonitrile, polybutadiene, acrylonitrile-containing rubbers, styrene-acrylonitrile copolymer and polyphenylene oxide.

The polyamides may be linear or crosslinked. A cross-linked polyamide provides some improvement in mechanical properties, particularly impact strength, but linear polyamides are also definitely included within the scope of this invention. The maximum amount of tolerable crosslinking in the polymer depends upon the proposed use of the finished composition. Moderate crosslinking produces compositions with high impact resistance and somewhat diminished flexural strength and modulus. Consequently, control of crosslinking provides a variable which enables one to "tailor" the polyamide in many respects to produce a composition of the desired properties. Suitable crosslinking agents are well known in the art and can be used here in the conventional manner. Two compounds which we have used include polyethyleneimine and tetra-(3-aminopropoxymethyl)methane. In addition, crosslinking can be achieved through a coupling agent, as described herein, by hydrolysis of silanol groups to form siloxane linkages, i.e.



or by the use of polyfunctional promoters in a lactam polymerization, such as di- and triisocyanates or by the inclusion of polymers such as polyisopropyl acrylamide or polymethyl methacrylate.

Polymer compositions of this invention necessarily contain less than 80% by volume of polyamide resin binder. This is because at least 20% by volume of filler must be present. The compositions preferably contain at least 10% and more preferably at least 20%, by

volume of polyamide resin. Also included in this invention are composites consisting of, for example, 98% or more of woven glass mats held together in laminated form by 2% polyamide resin binder.

5 The term "filler" as used herein refers to normally solid, nonpolymerisable material capable of existing and remaining in a different phase for the polymer, or polymerising monomer, when subjected to processing conditions necessary to shape the filler-containing polymeric basis. The filler may exist as discrete particles, as flakes or in woven fibrous form. The term *reinforcing adduct* refers to the reaction product of an inorganic filler with a coupling agent.

10 Inorganic fillers useful herein can be selected from a wide variety of minerals, metals, metal oxides, metal salts such as metal aluminates and metal silicates, other siliceous materials and mixtures thereof. To function effectively under conditions of high moisture, it is preferable that the filler be at most sparingly soluble in water, not exceeding a solubility of 0.5 gram per liter. If, however, the finished composition is to be used in an application where moisture sensitivity is not a problem, more soluble filler materials can be used. Generally, those hard, high modulus materials which have or can acquire an alkaline surface upon treatment with a base are well suited for our polymeric compositions. By high modulus is meant a Young's modulus of elasticity at least twice as great as that of the base polyamide. More preferably, suitable inorganic fillers will have a Young's modulus of 10^7 psi or greater. Many inorganic fillers fulfil both preferred characteristics of high modulus and alkaline surface and therefore constitute one class of preferred filler materials. Since metal silicates and siliceous materials usually have or can readily acquire the desired alkaline surface, and since they are characterized by modulus values well above the preferred minimum, a preferred mixture is one which contains a major amount, i.e. more than 50% by weight, of metal silicates or siliceous materials of the adduct.

Materials with such characteristics are preferred because of the ease with which they are coupled to the polymer as described subsequently herein. However, other substances such as alumina, Al_2O_3 , which are not easily coupled to a polyamide by means of coupling agents employed herein, can nevertheless be used as a reinforcing component either singly or preferably combined with other material which are more susceptible to coupling, and more preferably combined in minor amounts, i.e. percentages of less than 50% by weight of the total filler material. An example of such a material useful in the production of a reinforcing adduct with which alumina can be mixed, is feldspar. Feldspar can be converted into one of the preferred reinforcing adducts used in this invention and a feldspar-alumina

mixture is also useful. Other materials particularly preferred for conversion into reinforcing adducts include wollastonite, which is a calcium metasilicate; mullite, an aluminium silicate; calcium magnesium silicates; and an acicular aluminium silicate, Al_2SiO_5 . Other useful inorganic fillers which can be converted into reinforcing agents include quartz and other forms of silica such as silica gel, glass fibers and flakes, asbestos, carbon black, graphite, cristobalite and calcium carbonate; metals such as aluminium, tin, lead, magnesium, calcium, strontium, barium, titanium, zirconium, vanadium, chromium, manganese, iron, cobalt, nickel, copper and zinc; metal oxides in general such as oxides of the foregoing metals; heavy metal phosphates, sulfides and sulfates, and basic mineral and mineral salts such as spodumene, mica, montmorillonite, kaolinite, calcined kaolin clay, bentonite, hectorite, beidellite, attapulgite, chrysolite, garnet, saponite and Hercynite.

The term "*inorganic filler material*" or "*inorganic*" used in this disclosure refers to materials such as exemplified above which are as yet unmodified by reaction with a coupling agent. It should be noted that carbon black and graphite have been listed as suitable inorganic fillers. The term *inorganic*, in addition to conventional inorganic materials, also includes materials consisting predominately of elemental carbon. Particularly preferred are those inorganic siliceous materials which are characterized by a somewhat refractory nature with a melting point above about $800^\circ C$, a Moh's hardness of at least 4, and a water solubility of less than 0.1 gram per liter. Examples of preferred siliceous materials include minerals such as feldspar, quartz, wollastonite, mullite, kyanite, chrysolite, cristobalite, crocidolite, acicular aluminium silicate having the formula Al_2SiO_5 , spodumene and garnet. These minerals are especially desirable for use in reinforced polyamide compositions for a number of reasons. For instance, they provide a composition with better abrasion resistance, flexural strength and modulus, tensile strength and modulus, impact resistance, resistance to heat distortion and resistance to thermal expansion than do conventional clay fillers and inorganic pigments such as whiting. Further, the minerals described above provide higher loading levels than can be achieved with glass fibers, an important economic consideration. In addition, highly loaded lactam monomer slurries can be directly cast into a final polymerized form, thereby eliminating several processing steps necessary with glass fiber-reinforced compositions.

Metals have also been suggested as fillers. In addition to providing high strength, reinforced polymeric compositions, the use of certain metals such as copper, silver, iron and others can provide certain important auxiliary advantages. Moderate to high concentrations of

metals can make the polymeric composite electrically conductive, thereby rendering the composite suitable for an electroplating operation wherein the composite can be electroplated with a thin coat of a metal such as chromium, silver or gold. Or the use of iron or steel as a filler can give the polymeric composite magnetic properties if the particles are oriented within the composition.

In organic filler materials preferred herein are referred to as particulate. The term *particulate* as used in this disclosure refers to granular, plate-like and acicular particles having a length to diameter ratio (1/d) up to 25 to 1. Preferably, the inorganic fillers useful herein have an 1/d ratio up to 20 to 1, and more preferably up to 15 to 1. In contrast, the term *fibrous* refers to particles whose 1/d ratios are greater than 25 to 1, and usually are greater than 50 to 1. Fibrous fillers are also useful in the practice of this invention. Although the fillers can vary in shape from granular through acicular to plate-like and fibrous, dispersion in a polymer will require that the filler be small enough to be encapsulated by the polymer matrix forming the finished object. For instance, if the finished article has a thickness of 0.25 inch, the filler should have at least one dimension not exceeding about 0.25 inch.

The filler must comprise at least 20% by volume of the total composition. At lesser concentrations, the flame resistance of the resultant article is significantly diminished. More specifically, the flame resistance is impaired to such an extent that compositions containing less than 20 volume % filler cannot pass the test used herein to measure satisfactory flame resistance, even though the fire retardant material is used in the maximum concentration allowable within the scope of this invention.

Preferred filler concentrations are from 25 to 90 volume percent. When the filler is predominantly particulate in nature, particularly preferred concentrations of filler are from 33 to 67% by volume of the total composition. If fibres are used as part or all of the filler, preferred concentrations vary depending upon the size of the fibres and upon the method of incorporation into the resin matrix. If woven or random mats are saturated with a solution of resin to form a finished product, the filler content can be very high, on the order of 98% or more of the total composition. If random fibres are used as a filler and are incorporated into a monomer system which is to be cast into a mold for polymerization, the filler content must be far less if pourability of the mixture is to be retained. However, the filler content must nevertheless be at least 20 volume percent.

When superior mechanical properties are an important feature composition according to this invention contains a coupling agent. The coupling agents are polyfunctional compounds having at least one functional group capable of reacting with hydroxyl groups and at least one

functional group capable of reacting with a polymer or monomer in this case a polyamide or lactam monomer. A preferred class of coupling agents is an organosilane of the formula



where X is a hydrolyzable group capable of reaction with a hydroxyl group, Y is hydrogen or a monovalent hydrocarbon group, R is an alkylene group having from 1 to 20 carbon atoms, Z is a group capable of reaction with the polyamide, n is 0 or 1, a is 1, 2 or 3, b is 0, 1 or 2, c is 1, 2 or 3, and the sum of a + b + c equals 4.

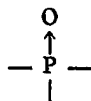
Examples of suitable X groups include halogen, hydroxy, alkoxy, cycloalkoxy, aryloxy, alkoxy-substituted alkoxy such as β -methoxy ethoxy, alkoxycarbonyl, aryloxy-carbonyl, alkyl carboxylate and aryl carboxylate groups, preferably having eight or less carbon atoms. Examples of Y groups in the above formula are hydrogen, methyl, ethyl, vinyl, isobutyl, and other hydrocarbyl groups, preferably having ten or less carbon atoms. The function of the Y group can be to modify the extent of the polymer-filler bond, to regulate viscosity of the monomer slurry or polymer mix or to modify the thermal stability of the coupler. The R group can be any alkylene group having up to 20 carbon atoms and preferably from 2 to 18 carbon atoms; examples include ethylene, propylene, decylene, undecylene and octadecylene. Further, the R group need not necessarily be present at all as indicated by the value of zero for the letter n. For instance, vinyl-substituted silanes are effective couplers. In such an instance, the vinyl group which is a Z group, is attached directly to the silicon atom. Usually, however, the Z group is separated from the silicon atom by an R group having at least two carbon atoms in the linking chain. As the number of carbon atoms in the R group increases, the coupler can perform as a viscosity reducer. Further, the activity of the Z group on the alkylene chain is often modified somewhat, thereby making the coupler perform more suitably under some processing conditions. The Z group can be any functional group capable of reacting with a polyamide. Examples include amino, primary or secondary amido, epoxy, isocyanato, hydroxy alkoxy-carbonyl, aryloxy-carbonyl, vinyl allyl and halogen such as chloro and bromo groups.

Thus as a further feature of the invention there is provided a flame retardant polymer composition comprising a polyamide homopolymer from 25% to 90% by volume of a inorganic filler, an organosilane coupling agent of the formula specified and from 10% to 35% by weight of the polyamide of polyhalogenated aromatic hydrocarbon.

Examples of suggested silane couplers include:

- vinyl triethoxysilane, $\text{CH}_2=\text{CHSi}(\text{OC}_2\text{H}_5)_3$;
 vinyl trimethoxysilane, $\text{CH}_2=\text{CHSi}(\text{OCH}_3)_3$;
 vinyl methylchlorosilane,
 $\text{CH}_2=\text{CHSi}(\text{CH}_3)\text{Cl}_2$;
 5 vinyl tri(β -methoxyethoxy)silane,
 $\text{CH}_2=\text{CHSi}(\text{OC}_2\text{H}_4\text{OCH}_3)_3$;
 methyl β -(methylchlorosilyl)acrylate
 $(\text{F}_3\text{CH}_2)_3\text{SiCH}=\text{CHCOOCH}_3$;
 2-(trimethoxysilyl)ethyl methacrylate,
 $(\text{CH}_3\text{O})_3\text{SiC}_2\text{H}_4\text{OOC}(\text{CH}_3)=\text{CH}_2$;
 10 3-(triethoxysilyl)propyl methacrylate,
 $(\text{C}_2\text{H}_5\text{O})_3\text{SiC}_3\text{H}_6\text{OOC}(\text{CH}_3)=\text{CH}_2$;
 4-(trichlorosilyl)butyl acrylate
 $(\text{Cl})_3\text{SiC}_4\text{H}_9\text{OOCCH}=\text{CH}_2$;
 15 6-(tricyclohexoxysilyl)hexyl methacrylate,
 $(\text{C}_6\text{H}_{11}\text{O})_3\text{SiC}_6\text{H}_{12}\text{OOC}(\text{CH}_3)=\text{CH}_2$;
 11-(trimethoxysilyl)undecyl methacrylate,
 $(\text{CH}_3\text{O})_3\text{SiC}_{11}\text{H}_{22}\text{OOC}-\text{C}(\text{CH}_3)=\text{CH}_2$;
 18-(triethoxysilyl)octadecyl acrylate,
 $(\text{CH}_3\text{O})_3\text{SiC}_{11}\text{H}_{22}\text{OOC}-\text{C}(\text{CH}_3)=\text{CH}_2$;
 20 18-(triethoxysilyl)octadecyl acrylate,
 $(\text{CH}_3\text{COO})_3\text{SiC}_{18}\text{H}_{36}\text{OOCCH}=\text{CH}_2$;
 p-[3-trimethoxysilylpropyl]styrene,
 $(\text{CH}_3\text{O})_3\text{SiC}_3\text{H}_6\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$;
 25 3-(triethoxysilyl)propyl chloride,
 $(\text{C}_2\text{H}_5\text{O})_3\text{SiC}_3\text{H}_6\text{Cl}$;
 11-(trimethoxysilyl)undecyl bromide,
 $(\text{CH}_3\text{O})_3\text{SiC}_{11}\text{H}_{22}\text{Br}$;
 ethyl β -triethoxysilyl propionate,
 $(\text{C}_2\text{H}_5\text{O})_3\text{SiC}_2\text{H}_4\text{COOC}_2\text{H}_5$;
 30 methyl ω -trimethoxysilyl undecylate,
 $(\text{CH}_3\text{O})_3\text{SiC}_{10}\text{H}_{20}\text{COOCH}_3$;
 glycidoxypentyl trimethoxysilane

$$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ (\text{CH}_3\text{O})_3\text{SiC}_5\text{H}_9\text{OCH}_2\text{CH}-\text{CH}_2 \end{array}$$
;
 35 trimethoxysilyl-3, 4-epoxycyclohexane,
 $(\text{CH}_3\text{O})_3\text{SiC}_6\text{H}_9\text{O}$;
 N-trimethoxysilylpropyl amine,
 $(\text{C}_2\text{H}_5\text{O})_3\text{SiC}_3\text{H}_6\text{NH}_2$;
 N - trimethoxysilylpropyl - N(β - aminoethyl)
 amine,
 $(\text{CH}_3\text{O})_3\text{SiC}_3\text{H}_6\text{NHC}_2\text{H}_4\text{NH}_2$; and
 N-trimethoxysilylundecyl amine,
 $(\text{CH}_3\text{O})_3\text{SiC}_{11}\text{H}_{22}\text{NH}_2$.
 Other classes of coupling agents can also be
 45 used. Polyfunctional compounds organized in
 a structural form and having functional groups
 similar to the above silanes but having a phos-
 phorus atom or phosphonyl group, i.e.



- 50 instead of the silicon atom are acceptable
 coupling agents. Specific examples; as well as
 a general description of such couplers are
 disclosed in U.S. Patent 3,344,107. Other
 acceptable coupling agents include complexed
 55 coordinate chromium compounds such as
 amino-chromic chlorides and isocyanate com-
 pounds such as 3-hydroxypropyl isocyanate,
 and amino compounds such as 5,6-dihydroxy-

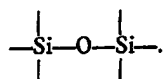
hexylamine. There exists a large body of art
 describing various means of treating fillers to
 increase their adherence to a resin matrix. It
 is our intent to include all such treating agents
 containing the requisite polyfunctionality
 described above.

It can be considered, as a working hypo-
 thesis, that chemical bonds are formed between
 polymer and coupler and between coupler and
 filler. Those couplers which have functional
 groups capable of such reactions provide com-
 positions with excellent properties whereas
 couplers not containing such functional groups
 generally provide compositions with inferior
 properties. It is believed that the adhesion of
 polymer to filler involves dual considerations.
 The first consideration is the polymer-coupler
 interface. Adhesion of polymer and coupler
 can be achieved under any conditions which
 permit thorough contact of the two com-
 ponents. One means has been to mix the
 coupler and filler with the polyamide-forming
 monomers and conduct a polymerization.
 Another means has been to mix thoroughly a
 coupler, filler and preformed polymer. Other
 techniques which provide the requisite contact
 of polymer and coupler can also be used.
 Reaction can occur by several mechanisms such
 as aminolysis, alcoholysis, ester interchange
 and alkylation. Aminolysis can occur by reaction
 of amino groups or by amide interchange with
 primary or secondary amido groups with the
 amide groups of the polymer. Ester interchange
 can occur by the reaction of esters with the
 amide group of the polymer. Alkylation can
 occur by a reaction where an ethlenically
 unsaturated group reacts with the amide group
 of the polymer. Alcoholysis can take place by
 the reaction of hydroxyl groups with an amide
 group. Additional reactions of amide groups
 with other functional groups are also known
 and can be used herein to provide the degree of
 adhesion of polymer to filler which forms the
 basis of the present invention. It should be
 noted in connection with the above comments
 on polyamide-functional group reaction that
 neither complete nor instantaneous reaction
 may be necessary. That is, if covalent bonding
 of polymer and coupler is responsible for the
 improvement achieved by the practice of this
 invention, it is further theorized that only a
 fraction of the possible polymer-coupler bonds
 may provide as good or nearly as good prop-
 erties in the finished composition as would a
 complete reaction.

The second consideration regarding the
 adhesion of polymer and filler is the coupler-
 filler interface. Filler and coupler can be joined
 by combining them in the absence or presence
 of a solvent for the coupler, such as water,
 alcohol, dioxane or benzene. Presumably, the
 hydrolyzable group to the coupler reacts with
 appended hydroxyl groups attached to the
 alkaline surface of inorganic materials.
 Theoretically, hydroxyl groups are present on

the surface of, or can be developed on the surface of, most metallic and siliceous substances, thereby providing a site available for reaction with a hydrolyzable group of a coupler. This theory of availability of hydroxyl groups on an inorganic surface may explain why many silicon-containing minerals are preferred reinforcing agents and why silicon-based coupling agents are particularly preferred for use with the siliceous minerals, i.e. the silane groups of the coupler —Si—(OR)_3 , react with

the silanol groups of the inorganic —Si—OH ,
to produce the very stable siloxane linkage,



If the above theory is accurate, chemical bonding of coupler to the inorganic filler is achieved in the compositions of the present invention. Other theories can be advanced which deny the existence of true covalent bonds between inorganic filler and coupler. Regardless of any theoretical explanation advanced herein, the coupler is attached to the inorganic filler by contacting the two substances. The mixture is preferably but not necessarily, subsequently dried. A bond between the inorganic filler and coupler is thus obtained. The reaction of filler and coupler can be carried out separately, and the filler-coupler adduct subsequently added to the monomer, or preformed polymer, or the reaction may be carried out in the presence of the monomer or polymer and the whole mixture dried to remove volatile reaction products and solvents, if used. Preferably, heat in the range of 50 to 200°C is applied to a coupler-filler adduct to increase the extent of bonding.

The amount of coupler with which the inorganic filler is treated is relatively small. As little as one gram of coupling agent per 1000 grams of filler produces a polymer composition with mechanical properties superior to those of a polymer composition containing an untreated filler. Generally, quantities of coupler in the range of 2.0 to 40.0 grams per 1000 grams of reinforcing agent have been found most satisfactory although quantities in excess of that range may also be used.

The polyhalogenated aromatic hydrocarbons used in the present invention may also be admixed with antimony oxides and hydrocarbyl phosphate esters and mixtures thereof. The term "hydrocarbyl" is used herein to indicate any monovalent hydrocarbon or substituted hydrocarbon group. Particularly advantageous substituents are the halogens such as chlorine and bromine, and hydroxy groups. Examples of suitable compounds are antimony trioxide, antimony tetraoxide, antimony pentaoxide, tritoyl phosphates, triphenyl phosphates, ditoyl phosphates, tolyldiphenyl phosphonates,

diphenyl octyl phosphate tri(dichloropropyl)-phosphate, tri(dibromopropyl)phosphate, tributyl phosphate, tris-(β -chloroethyl)-phosphate, bis-(dibromopropyl)phosphate, dichloropropyldivinyl phosphate, which may be used in admixture with a polyhalogenated aromatic hydrocarbon, for example halogenated biphenyl, tri-phenyl and other polyphenyl such as tetrachlorobiphenyl and monobromopentachlorotriphenyl, dichlorotoluene, tetrabromobenzene and, β,β' -dichloro-p-xylene.

A particularly preferred mixture for use according to the invention is a mixture of an antimony oxide with the polyhalogenated aromatic hydrocarbon. Such a mixture definitely exerts a multisynergistic action. The mixture is an effective flame retardant at a concentration lower than can be used with either component alone.

Secondly, polyamide compositions modified by the above mixture, in addition to acquiring good flame resistance, also retain a very satisfactory level of mechanical properties, which is not possible in polyamide compositions flame proofed with a single component additive.

Amounts of polyhalogenated aromatic hydrocarbon necessary to achieve non-flammability as measured herein vary somewhat depending upon the type of material or mixture of materials used, the amount of filler and size of filler particles and other factors. It has been found that the polyhalogenated aromatic hydrocarbon must be present in a concentration from 8% to 35% by weight of the polyamide resin matrix. In a composition containing 40% or 45% by volume of 10 μ quartz silica, a preferred concentration range of flame retardant is from 10% to 35% by weight of the polyamide. It should also be recognized that certain flame retardants are more effective than others. For instance, a 50:50 mixture of antimony trioxide and chlorinated bi- and tri-phenyls in a concentration of 25% by weight of the resin is a very effective flame retardant in a composition containing 70% by volume inorganic filler of 20 μ average particle size.

Flame retardance of polymeric compositions according to this invention can be measurably enhanced by equilibrating the samples with atmospheric moisture. Polyamides tend to absorb water through the formation of hydrogen bonds. The process is somewhat slow however depending upon atmospheric conditions and the surface area of the polymeric article. A filled polyamide sheet $\frac{1}{8}$ inch thick at 25°C and 50% relative humidity will usually require several weeks to become fully equilibrated with the atmosphere. Water equilibration can be accelerated by placing the samples in an atmosphere of high humidity and temperature. Three days in boiling water followed by one day in a normal atmosphere provides fully equilibrated reinforced polyamide compositions.

In addition to the foregoing components, a number of other materials may be present in

the compositions of this invention. Stabilizers, dyes, pigments, crosslinking agents, mold release agents, dispersing aids and several other materials can be added, sometimes in substantial quantities. For instance, when filler concentration approaches 80% by volume, an appreciable quantity of a tetraalkylorthosilicate can be helpful as a dispersing aid and as a mold release agent. In some applications, it may be desirable to cast a polymerizable mixture of this invention onto or into a woven or random glass mat to provide an article with an exceptionally high inorganic content and good flame-retardant properties. Or it may be desirable to cast the polymerizable mixture into or onto some combustible substance to provide a hard, wear-resistant, fire-resistant article. Several other materials can be added to compositions of this invention to alter substantially their final form, shape or utility without adversely affecting the flame-retardant characteristics of the compositions.

The compositions of this invention can be prepared in a number of ways. For instance, a polyamide resin unmodified by filler, coupler or polyhalogenated aromatic hydrocarbon can be mixed with the requisite amounts of filler treated with a coupler, and polyhalogenated aromatic hydrocarbon in an extruder or injection molding machine to yield the desired product. The components of the composition can be added sequentially in any order or they can be mixed together simultaneously. Similarly, the reaction conditions can vary widely. That is, the components can be mixed together at room temperature and atmospheric pressure, formed into pellets or granules and then fabricated into useful shapes by any conventional molding technique or the various additives can be added to a molten polyamide or polyamide solution just prior to the fabrication step. Another method of preparation is to incorporate any of the above additives into the monomer system before it is polymerized. As an example, the polyhalogenated aromatic hydrocarbon, filler, coupler, and other additives such as stabilizers, dyes and pigments can be added individually or collectively to the monomer system which can then be subsequently polymerized, at which time other additives can be added prior to a subsequent forming operation. In general any of the polymerization and fabricating techniques applicable to polyamides can be used here to prepare the composition of the invention, including in the *in situ* polymerization casting of polyamides by the base-catalysed, substantially anhydrous polymerization of lactams. Polymerization casting of a finished article directly from a mixture of easily handled components has definite advantages of simplicity and economy.

Another feature of this invention is directed to a process for preparing the flame-retardant compositions of the inventions. The process comprises preparing a flame-retardant polymer

composition of the invention wherein a mixture containing a monomeric lactam and capable of being polymerised to form component (a), at least 20% by volume of an inorganic filler and from 8% to 35% by weight of the lactam of a polyhalogenated aromatic hydrocarbon, or a mixture thereof with antimony trioxide, is prepared and subjected to a base-catalysed, substantially anhydrous polymerization of the lactam. Polymerizations are conducted according to conventional techniques well known in the art. Polymerization times and temperatures, catalysts, initiators, regulators and other additives are amply described in U.S. Patent Nos. 3,017,391; 3,017,392; 3,018,273 and 3,028,369. Preferred embodiments often use a polymerization temperature of from 140 to 200°C and a polymerization time of from 1 to 10 minutes, depending upon catalyst and initiator type and concentration. Preferred catalysts include the alkali lactams such as sodium caprolactam and the Grignard reagents such as ethyl magnesium bromide. Preferred initiators include the acyl lactams, such as acetyl caprolactam and the organic isocyanates such as phenyl isocyanate and toluene diisocyanate. Other operative and preferred ranges of component materials are similar to those described above for the polyamide compositions. One procedure suitable for preparing flame-retardant reinforced polyamides comprises first mixing the lactam monomer, filler, polyhalogenated aromatic hydrocarbon and, if desired, a crosslinking agent, internal mold-releasing agent, stabilizer or other additives. Mixing is most effectively carried out if the lactam is in a molten condition. When high concentrations of filler are used, e.g. 35 or 48% by volume or more, it may be advisable to add the components in the order just given in order to disperse effectively the ingredients. After thorough mixing, the mixture is heated to between 110 and 160°C, but preferably to between 110°C—120°C, to remove water or other volatile materials. A vacuum can be applied to this end. The temperature of the mixture is then adjusted to some temperature above the melting point of the lactam, about 100°C for ϵ -caprolactam, and the polymerization catalyst is added. If a Grignard reagent is used, the temperature of the mixture is held around 100°C to permit volatilization of the alkane formed by the reaction of the Grignard with the lactam monomer. Following addition of the catalyst and removal of volatile reaction products, if necessary, the promoter or initiator is added. Any of the promoters useful in base-catalyzed lactam polymerizations can be used. Examples include carbon monoxide, acetyl caprolactam, diisopropylcarbodiimide, dicyclohexylcarbodiimide and N,N-diphenylcyanamide. Other suitable promoters include lactams having attached to the imido group a heterocyclic constituent containing from 1 to 3 heterocyclic atoms, wherein at least one of

the heterocyclic atoms is a nitrogen atom and wherein the imido group of the lactam is attached to the carbon atom in the heterocyclic ring so situated that the nitrogen of the imido group and the nitrogen of the heterocyclic ring are connected by an odd number of conjugated carbon atoms. Examples of this class of promoters include N-(2-pyridyl)- ϵ -caprolactam, N-(4-pyridyl)- ϵ -caprolactam, tris-N-(2,4,6-triazino)- ϵ -caprolactam and N-(2-pyrazinyl)- ϵ -caprolactam. These promoters can be formed by the *in situ* reaction of a lactam with such compounds as 2-chloropyridine, 4-bromopyridine, 2-bromopyrazine, 2-methoxypyridine, 2-methoxypyrazine, 2,4,6-trichloro-s-triazine, 2-bromo-4,6-dichloro-s-triazine and 2,4-dimethoxy-6-chloro-s-triazine. Alternately, the promoter may be added before the catalyst. Whichever procedure is followed, once the mixture contains the monomer, the promoter and catalyst, for most systems it is necessary to keep the temperature below 140°C, preferably below 120°C, to prevent too rapid polymerization until the mixture is cast. Some catalyst-promoter systems, such as the alkyl magnesium chloride-acetyl caprolactam system, will require even a further reduction in heat to less than 80°C to prevent polymerization. It is also advisable when employing a reactive catalyst-promoter system to reduce the time intervening between the addition of the catalyst-promoter and the casting or molding of the mixture. After the mixture has been thoroughly stirred and allowed to come to equilibrium, the mixture is cast into a mold, which is separately preheated, and polymerized at a temperature from about the melting point of the lactam up to about 250°C preferably from about 140°C to about 200°C. Time for polymerization can vary for example from one minute to an hour and usually requires from 2 or 3 minutes up to 10 minutes with most preferred catalyst-promoter systems. Other lengths of time and temperatures for polymerization are of course satisfactory and can be used with equal or nearly equal success.

When the filler is treated with a coupling agent, rapid polymerizations are readily achieved without further coupler treatment. In the absence of a coupling agent, the filler usually acts to slow down or inhibit the polymerization, especially if it contains a large amount of absorbed or adsorbed water. A preferred method of using a coupling agent in a base-catalyzed polymerization is to place it in the presence of filler before the polymerization catalyst or initiator is added.

Chemical additives other than catalyst or initiator added to react with a filler surface are preferably reacted with the filler prior to addition of the catalyst or initiator.

In addition to the foregoing polymerization process, several alternate methods of *in situ* polymerizations are available. For instance,

addition of flame retardant or filler to the polymerization mixture can be withheld until just prior to casting. Instead of casting the mixture into a closed stationary mold, it can be cast onto a moving belt or into a rotating mold. Other techniques within the skill of competent artisans can also be employed herein.

The invention will be more clearly understood from a detailed description of the following specific examples which set forth some of the preferred compositions, methods for their preparation, and some of the advantages attained by the practice of this invention. Quantities of materials are expressed in parts by weight except as otherwise specifically noted.

EXAMPLE 1

To 550 parts of molten ϵ -caprolactam are added 2870 parts of flintshot, 1170 parts of quartz silica, 12 parts of 3-triethoxysilylpropylamine and 45 parts of antimony trioxide. The mixture is thoroughly dispersed and heated to 160°C under vacuum to remove volatile reaction products. The heating is continued until 50 parts of caprolactam are removed. To the mixture is then added a quantity of toluene diisocyanate sufficient to provide 9 millimoles of isocyanate per mole of caprolactam. The mixture is heated to 140°C under vacuum for three or four minutes, after which time the vacuum is released and 135 parts of 1,2,4,5-tetrabromobenzene are added. After dispersing the tetrabromobenzene, ethylmagnesium bromide in a concentration sufficient to provide seven millimoles of the Grignard reagent per mole of caprolactam is added to the mixture. A vacuum is applied for two or three minutes and the mixture is then cast into a sheet mold $\frac{1}{8}$ inch thick which is preheated to 150°C. The mold is maintained at this temperature for ten minutes, after which time the mold is opened to yield a solid polymerized product having 77 volume % filler.

Testing for flame retardancy is carried out in the following manner. Sample specimens having dimensions of $3 \times \frac{1}{2} \times \frac{1}{8}$ inches are cut and hung vertically in a draftless area. The tip of a Bunsen burner flame is adjusted to a $\frac{1}{2}$ inch high cone and held at the lower edge of a specimen at an angle of 20° from the vertical for a period of ten seconds (the first heating period). The flame is removed and after an additional thirty seconds, the flame is brought back for another ten second heating period (the second heating period).

Compositions prepared according to Example 1 do not inflame during the first heating period but do inflame during the second heating period.

Sample specimens of compositions prepared according to Example 1 are water-equilibrated by placing them in boiling water for 72 hours. Samples water-equilibrated in this manner do

not inflame even after the second heating period.

EXAMPLE 2

The procedure described in Example 1 is followed exactly except that neither antimony trioxide nor 1,2,4,5-tetrabromobenzene is added to the polymerization mixture. Whether or not water-equilibrated, the compositions catch fire during the first heating period.

EXAMPLE 3

The procedure described in Example 1 is followed except that in place of the mixture of flintshot and silica, 250 parts of 325 (U.S.S. sieve size) mesh silica are used. Further, 175 parts of a chlorinated polyphenyl (Aroclor Registered Trade Mark) are used in place of the bromobenzene. The finished composition contains 17% by volume inorganic filler. Whether or not water-equilibrated, sample specimens inflame readily during the first heating period.

"Aroclor" is a chlorinated biphenyl containing approximately 42% by weight of chlorine corresponding to a predominance of trichlorobiphenyl.

EXAMPLE 4

The procedure described in Example 3 is followed except that 350 grams instead of 250 grams of silica are used. The final composition contains 21% by volume filler. When tested for flame retardancy, the dry samples do not inflame during the first heating period but they do inflame during the second period. Similarly, water-equilibrated samples do not inflame during the first heating period. During the second period, they inflame.

EXAMPLE 5

To 500 parts of nylon 6,6 is added 40 parts of antimony trioxide and 160 parts of a chlorinated polyphenyl compound (Aroclor). The mixture is extruded into $\frac{1}{8}$ inch thick sheets for flame retardancy testing. Whether or not the samples are water-equilibrated, the samples inflame readily during the first heating period.

EXAMPLE 6

The procedure of Example 5 is followed except that nylon 6, polycaprolactam, is used instead of the nylon 6,6. Both the water equilibrated and non equilibrated samples inflame readily during the first heating period.

EXAMPLE 7

To 500 parts of nylon 6,6 are added 4500 parts of 325 mesh quartz silica pretreated with 20 parts of 3-triethoxysilylpropylamine. The mixture is extruded into $\frac{1}{8}$ inch thick sheets containing 78% by volume filler. Whether or not water-equilibrated, the samples inflame readily during the first heating period.

EXAMPLE 8

To 525 parts of molten ϵ -caprolactam are added 100 parts of a 50:50 mixture of wollastonite and calcined kaolin clay which has been pretreated with 4 parts of methyl 11-trimethoxysilylundecanoate. To the monomer-filler slurry are added 10 millimoles of toluene diisocyanate per mole of caprolactam, 30 parts of antimony trioxide and 90 parts of monobromopentachlorotriphenyl. Following thorough mixing at 130°C under vacuum for 15 minutes during which time 25 parts of caprolactam are removed, 11 millimoles of sodium caprolactam are added and the mixture cast into a $\frac{1}{8}$ inch thick sheet mold preheated to 175°C. The mold is maintained at this temperature for 10 minutes after casting, after which time it is allowed to cool. The polymerised product is cut into sample specimens for flame retardancy testing. Dry samples withstood both heating periods without inflaming and the water-equilibrated samples also withstood both heating periods without inflaming.

EXAMPLE 9

To 500 parts of nylon 6,6 are added 900 parts of 325 mesh U.S.S. sieve size garnet, 4 parts of 3-triethoxysilylpropylamine, 10 parts of antimony trioxide and 30 parts of a chlorinated polyphenyl compound (Aroclor). The mixture is extruded into $\frac{1}{8}$ inch thick sheets for testing. Both the water-equilibrated and non-equilibrated samples withstood the first heating period and inflamed during the second period.

Testing results are summarised in the table below. Flame retardancy is reported according to the following legend:

- 0 = sample inflamed during the first heating period.
- 1 = sample did not inflame during the first heating period but did inflame during the second heating period.
- 2 = sample did not inflame during either heating period.

TABLE I

Polymeric Composition of Example No.	Filler Concentration volume %	Polyhalogenated Hydrocarbon and Antimony trioxide Wt. % of Polyamide	Water Equilibration	Flame Retardancy
1	77	35	no yes	1 2
2	77	0	no yes	0 0
3	17	35	no yes	0 0
4	21	35	no yes	1 1
5	0	40	no yes	0 0
6	0	40	no yes	0 0
7	78	0	no yes	0 0
8	45	24	no yes	2 2
9	36	8	no yes	1 1

Test results reported for Compositions 2 and 7 show that very high filler loadings alone do not impart any measurable flame resistance to polyamide compositions. This is demonstrated to be independent of whether the polyamide is nylon -6 or nylon -6,6; or whether or not the filler is incorporated with a coupling agent. Compositions 5 and 6 show that even larger quantities of polyhalogenated aromatic hydrocarbons alone are not capable of producing flame-resistance in polyamides. Comparison of compositions 1 and 2 shows that the combination in accordance with this invention of inorganic filler and polyhalogenated aromatic hydrocarbons provides good flame resistance. Composition 3 shows that less than 20% by volume of inorganic filler, even when used with an amount of polyhalogenated aromatic hydrocarbon as used in this invention, does not provide measurable flame resistance in a polyamide. Composition 4, containing the same amount of polyhalogenated aromatic hydrocarbon together with just above 20% by volume of inorganic filler, does have a measurable flame resistance. Compositions 8 and 9 show the use of various polyhalogenated aromatic hydrocarbons and demonstrate their utility. Compositions 1, 4, 8 and 9 provide representative example of flame-retardants

which are useful in the *in situ* base-catalyzed substantially anhydrous lactam polymerization.

We make no claim to a flame resistant polymer composition comprising, as polyhalogenated aromatic hydrocarbon, pentabromotoluene. Subject to the foregoing disclaimer.

WHAT WE CLAIM IS:—

1. A flame resistant polymer composition comprising:
 - (a) a polyamide;
 - (b) at least 20% by volume of the composition of an inorganic filler; and
 - (c) from 8% to 35% by weight of the polyamide of a polyhalogenated aromatic hydrocarbon, or a mixture thereof with antimony oxide.
2. A polymer composition according to claim 1 wherein the polyamide is a polylactam.
3. A polymer composition according to claim 2 wherein the polyamide is polycaprolactam.
4. A polymer composition according to claim 1 wherein the polyamide is polyhexamethylene adipamide.
5. A polymer composition according to claim 1 wherein the polyamide is a copolymer.
6. A polymer composition according to claim 1 wherein the polyamide is present in a

mixture containing at least 50% by weight of polyamide resins.

7. A polymer composition according to any of claims 1—6 wherein filler is present in a concentration from 25% to 90% by volume of the total composition.

8. A polymer composition according to any of claims 1—7 wherein said filler comprises more than 50% by weight of metal silicates or other silicious materials.

9. A flame resistant polymer composition according to claim 1 wherein the composition is made electrically conductive or magnetic by the addition of a filler comprising a suitable metal.

10. A polymer composition according to any of claims 1—9 wherein component (c) is present in a quantity from 10% to 35% by weight of the polyamide.

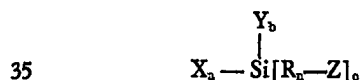
11. A polymer composition according to any of claims 1—10 wherein component (c) is a polyhalogenated polyphenyl compound.

12. A polymer composition according to any of claims 1—10 wherein component (c) is tetrabromobenzene.

13. A polymer composition according to any of the preceding claims which also comprises an antimony oxide.

14. A polymer composition according to any of claims 1—13 wherein the composition contains a coupling agent.

15. A polymer composition according to claim 14 wherein the coupling agent is an organosilane of the formula



where X is a hydrolyzable group capable of reaction with a hydroxyl group, Y is hydrogen or a monovalent hydrocarbon group, R is an alkylene group having from 1 to 20 carbon atoms, Z is a group capable of reaction with the polyamide n is 0 or 1, a is 1, 2 or 3, b is 0, 1 or 2, c is 1, 2 or 3, and the sum of a + b + c equals 4.

16. A flame resistant polymer composition according to claim 15 comprising a polyamide homopolymer, from 25% to 90% by volume

of an inorganic filler, an organosilane coupling agent as defined in claim 18 and from 10% to 35% by weight of the polyamide of a polyhalogenated aromatic hydrocarbon.

17. A process for the production of a flame resistant composition as defined in any of claims 1—16 which comprises forming an admixture of the ingredients specified in the proportions specified in any of the said claims.

18. A process according to claim 17 wherein the admixture of the ingredients is effected in an extruder or injection moulding machine and the composition obtained therefrom as an extruded or moulded product.

19. A process for the production of a flame resistant polymer composition according to any of claims 1 to 16 wherein a mixture containing a monomeric lactam and capable of being polymerised to form component (a), at least 20% by volume of an inorganic filler and from 8% to 35% by weight of the lactam of a polyhalogenated aromatic hydrocarbon, is prepared and subjected to a base-catalysed, substantially anhydrous polymerization of the lactam.

20. A process according to claim 19 wherein the inorganic filler is contacted with a coupling agent prior to its incorporation in the mixture.

21. A process according to either of claims 19 and 20 wherein the polymeric composition so formed is equilibrated with atmospheric moisture by boiling in water, and subsequently allowing the composition to equilibrate atmospheric moisture.

22. A process for preparing a composition according to claim 1, substantially as hereinbefore described with reference to the foregoing specific Examples 1, 4, 8 and 9.

23. A composition according to claim 1 substantially as hereinbefore described with reference to any of Examples 1, 4, 8 and 9.

24. A polyamide composition whenever prepared or produced by any of the processes of claims 17 to 22.

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